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Unexpected rearrangements in the synthesis of an unsymmetrical tridentate dianionic *N*-heterocyclic carbene†

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Starting from the same ethylenediamine species, three valuable carbene precursors were synthesized under differing conditions: a tridentate dianionic *N*-heterocyclic carbene bearing an aniline, a phenol and a central dihydroimidazolium salt, its benzimidazolium isomer by intramolecular rearrangement and a dicationic benzimidazolium-benzoxazolium salt by changing the Brønsted acid from HCl to HBF_4. A DFT study was performed to understand the rearrangement pathway. The structure of a bis[(NCO) carbene] zirconium complex was determined.

Introduction

N-Heterocyclic carbene (NHC) ligands have been extensively explored in late transition metal catalysis, frequently providing enhanced catalyst stability, activity and selectivity.[1] Recently, new generations of bidentate or tridentate NHC ligands have attracted attention, especially to access interesting chiral systems[2] and to isolate rare examples of carbene-early transition metal complexes.[3] Indeed, Hoveyda *et al.* reported the synthesis of chiral bidentate NHC-phenolate ligands, whose ruthenium complexes catalyze highly enantioselective ring-opening metathesis/cross-metathesis reactions.[2a] Moreover, several examples of early transition metal complexes with tridentate NHCs bearing anionic tethers have exhibited high activity in ring-opening polymerization of *rac*-lactide[4] and in olefin polymerization.[5] For such applications, dianionic tridentate ligands with the carbene donor in the central position are attractive candidates, forcing the binding of the soft NHC to the hard metal centre. Up to now, the only examples of such tridentate dianionic ligands have been reported with coordination patterns OCO (**A**),[5a,6] NCN (**B**),[5e,7] SCS (**C**),[8] and OCN (**D**)[9] (Chart 1). The alkoxide-NHC-amidate ligand **D**, the only unsymmetric version, is of particular interest because its complexes offer possibilities for stereoselective catalysis. In attempting the synthesis of a precursor to an example of **D** with anilide and aryloxide arms, we found that under certain conditions the imidazolium precursor undergoes an unexpected rearrangement, providing access to two other potentially useful NHC precursors. We also studied its coordination behavior on a zirconium complex.

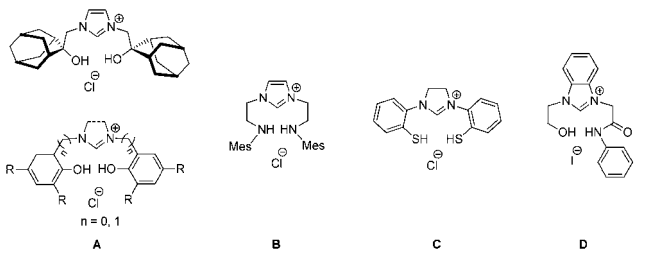

Chart 1 Tridentate dianionic NHC precursors.

Result and discussion

The target compound, phenol-aniline dihydroimidazolium **4**, was synthesized as shown in Scheme 1. Oxalamide **2**, obtained from 2-(*N*-mesitylamino)aniline and 2-amino-4,6-di-*tert*-butylphenol, was reduced by borane–THF or $LiAlH_4$ to *N*-(2-mesitylaminophenyl)-*N*′-(3,5-di-*tert*-butyl-2-hydroxyphenyl)-ethylenediamine (**3**). Heating the dihydrochloride salt of **3** with triethyl orthoformate for 15 minutes at 40 °C precipitated a white powder consisting of 3-(3,5-di-*tert*-butyl-2-hydroxyphenyl)-1-(2-(mesitylamino)phenyl)-4,5-dihydro-1*H*-imidazol-3-ium chloride (**4**), characterized by ^1H, ^{13}C, HSQC and NOESY NMR and elemental analysis.[10] In the ^1H NMR spectrum in $CDCl_3$ the methylene

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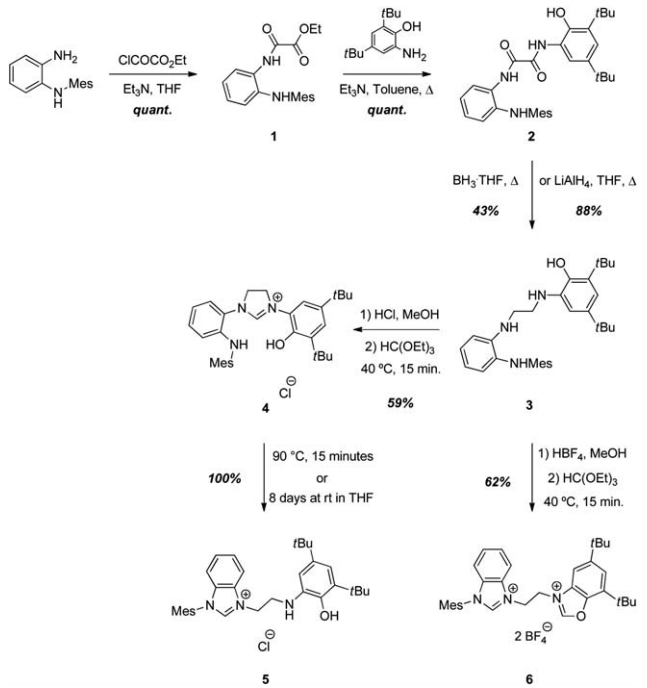
† Electronic supplementary information (ESI) available: Experimental details (synthesis and copies of ^1H and ^{13}C NMR), crystallographic data of **5–7** and computational details. CCDC 857560 and 862749. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3sc22171g



Scheme 1 Tridentate dianionic azolium synthesis.

protons of the imidazolium ring appear as one singlet (at 4.77 ppm), somewhat surprising in view of the unsymmetric substitution (for example, the analogous 1-mesityl-3-tolyl-4,5-dihydro-1*H*-imidazolium features two doublets in $CDCl_3$, at 4.62 and 4.91 ppm (ref. 11)). This coincidence of ^{1}H NMR resonance in $CDCl_3$ appears to be accidental; in MeOH at −40 °C two multiplets are observed, at 4.56 and 4.45 ppm.

Imidazolium **4** appears completely stable in the solid state, but in chloroform solution new ^{1}H and ^{13}C NMR signals begin to appear in a few days. Clean rearrangement to a new species, with no apparent byproducts, is essentially complete after 10 days at room temperature in chloroform (8 days in tetrahydrofuran); the same product can also be generated by heating **4** in toluene at 90 °C for 15 minutes. The product was identified by NMR as **5**,[12] and confirmed by an X-ray diffraction study of crystals obtained from an acetone/pentane solution (Fig. 1). This benzimidazolium NHC precursor results from the central carbon of the imidazolium ring of **4** "walking" down the molecule to a new position, between one of the central nitrogen centers and the original aniline nitrogen. A notable feature of the structure is the three hydrogen-bonding interactions of the chloride ion: Cl(l)···H(16)–C(16) (Cl(l)···C(16) = 3.33 Å, C(16)–H(16) = 0.95 Å, C(16)–H(16)–Cl(1) = 159°), Cl(1)···H(3A)–N(3) (Cl(1)···N(3) = 3.29 Å, N(3)–H(3A) = 0.87 Å, N(3)–H(3A)–Cl(1) = 166°), and Cl(1)···H(1)–O(1) (Cl(1)···O(1) = 3.09 Å, O(1)–H(1) = 0.89 Å, Cl(1)–H(1)–O(1) = 165°).

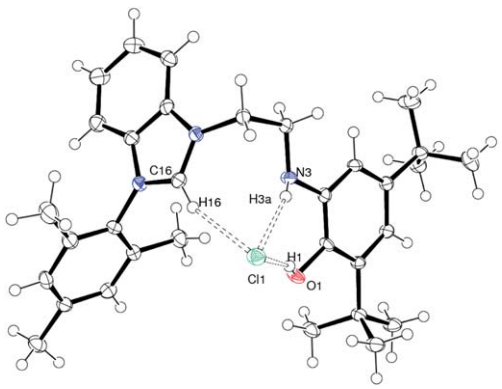


Fig. 1 Molecular structure of benzimidazolium **5**. Selected bond lengths (Å) and angles (°): C(16)–N(1) = 1.3366(19), C(16)–N(2) = 1.3294(19), N(1)–C(16)–N(2) = 109.98(15).

Previous examples of this type of tridentate dianionic benzimidazolium framework, containing amidate and chiral alkoxide groups, have been used to assemble catalysts that exhibit a variety of interesting properties, such as high enantioselectivities in intermolecular Heck-type coupling reactions,[13] enantioselectivity reversal in conjugate addition reactions,[14] and high enantioselectivity in Ir-catalyzed transfer hydrogenation.[15] (The C–O double bond of the amidate group is just a tool to aid synthesizing the ligand: only the nitrogen atom interacts with the metal centre.) Our new approach *via* rearrangement allows accessing this class of NHC-amino-phenol ligands with facile variation of aryl substituents. For example, a chiral version could be obtained starting from a chiral 1-alkyl-2-amino phenol compound.

A DFT study was performed to help explain the mechanism of this unprecedented rearrangement. Calculations were carried out in the gas phase at the B3LYP/6-31G**//M06-2X/6-31G** level of theory with the Gaussian 09 program[16] on model compound **4′** (without Cl^-) and **4″** (with Cl^-) in which Me replaces ^{t}Bu on the hydroxyphenyl group. Single point SMD calculations were also performed in order to take into account solvent (THF) effects (see ESI†).

Fig. 2 (values in black) presents the energy profile of the rearrangement from **4′** to **5′** without the counter-ion. Compound **5′** is found to be the thermodynamically preferred species, more stable than **4′** by about 15.8 kcal mol^{-1}. The calculations support a two-step pathway passing through a conformer **I′** located at the same energy as compound **4′** and having similar geometric parameters except for the rotational orientation of the aniline group (see ESI†), presumably to bring that N in a position to interact with the central C. The activation barrier of that first step is low (**4′** → **TS1′**: 12.6 kcal mol^{-1}) compared to the second one (**I** → **TS2′**: 32.1 kcal mol^{-1}). Transition state **TS2′** has structural features intermediate between those of **4′** and **5′**; it contains two fused five-membered rings with C(16)–N_{Mes}, C(16)–$N_{phenolate}$ and C(16)–N_{phenyl} distances of 1.513 Å, 1.528 Å and 1.445 Å respectively. The proton (shown as a small sphere), which moves from N(1) to N(3) is located approximately equidistant between the two nitrogen atoms (N(1)–H: 1.323 Å and N(3)–H: 1.356 Å) and at 1.726 Å from the C(16) carbon atom. The calculated overall barrier from **4′** to **5′** of 32.1 kcal mol^{-1} is much higher than that expected for full conversion in 15 minutes at 90 °C. The reasons are not obvious, except that the ion pairing and hydrogen bond interactions likely are major factors.

With the Cl^- counterion included (Fig. 2, values in red), product **5″** is still thermodynamically preferred over **4″**,

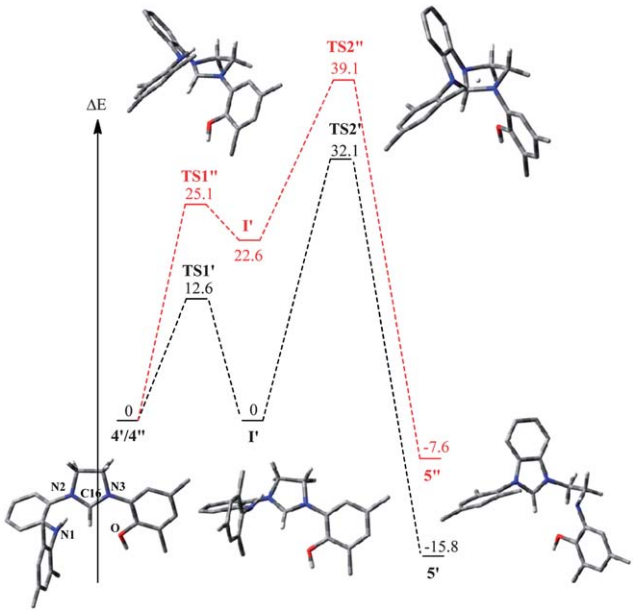


Fig. 2 Energy profile (energy in kcal mol^{-1}) computed at the B3LYP/6-31G**//M06-2X/6-31G** level of theory without the counter-anion (black) and with the counter-anion (red). Some hydrogens have been omitted for clarity.[19]

although by a smaller amount; but both conformer **I″** and the overall activation barrier are significantly higher in energy. On the other hand, the crystal structure of **5** shows stabilization by three Cl–H interactions; while those may result strictly from solid-state effects, they suggest at least the possibility that Cl^- could play a role in the rearrangement.

To examine the possible role of the anion in the rearrangement of **4**, the bis(ammonium) salt of **3** was generated using HBF_4 instead of HCl. When that was heated with triethyl orthoformate, following the same procedure as for imidazolium **4** (Scheme 1), a white powder again precipitated from solution, but its solubility and NMR properties were quite different from those of **4**.[17] Crystals were obtained from acetone/pentane at low temperature, and X-ray diffraction (Fig. 3) identified the product

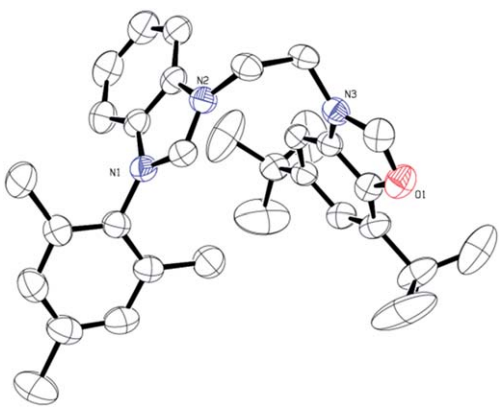
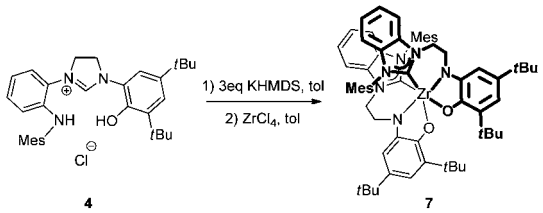


Fig. 3 Molecular structure of benzimidazolium-benzoxazolium bis-tetrafluoroborate **6**. Selected bond lengths (Å) and angles (°): N(1)–C(10) = 1.327(2), N(2)–C(10) = 1.321(2), N(3)–C(25) = 1.304(2), O(1)–C(25) = 1.305(3), N(1)–C(10)–N(2) = 110.93(19), N(3)–C(25)–O(1) = 113.0(2). The counter-anions BF_4^- have been omitted for clarity.

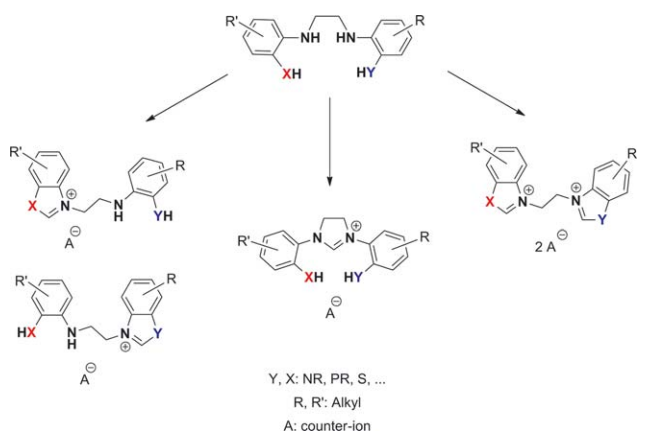


Scheme 2 Synthesis of (CNO)-zirconium complex **7**.

as benzimidazolium-benzoxazolium bis-tetrafluoroborate salt **6**. This appears to be the first example of a bis-NHC ligand containing an (NCN)–(NCO) linkage;[18] to our knowledge, only four reports of unsymmetrical dicarbenes have appeared, including some evidence for improved catalytic behavior.[20] The explanation for such a dramatic and unexpected effect of the counter-ion on the nature of the product may lie in the solubility of the monocationic salt: mono(tetrafluoroborate) salts tend to be more soluble than their chloride analogues, allowing them to react further with triethyl orthoformate.

We investigated the tris-deprotonation of the salt **4** with strong base (KHMDS) to generate the dianionic carbene *in situ* followed by its trapping on a zirconium complex (Scheme 2). After work-up, a red powder is obtained in 52% yield. In the ^1H NMR spectrum, the methylene protons range from 4.2 to 2.7 ppm as four multiplets, somewhat surprisingly dispersed for methylene protons in the *N*-heterocycle.[21] Nevertheless, the ^{13}C NMR spectrum shows the presence of one carbene signal at 200 ppm. Crystals were obtained from a toluene/pentane solution at low temperature and X-ray diffraction (see ESI†) identified the product as bis(benzimidazolylidene)zirconium complex **7**, resulting from the rearrangement of the imidazolyl unit to a benzimidazolyl moiety followed by bis-ligation. The zirconium metal center exhibits distorted *mer*-octahedral coordination of the two (CNO) carbene ligands with each NHC *trans* to its phenolate and the amide groups *trans* to one another.[22]

Thus, addition of base to salt **4** led to a benzimidazolylidene-type carbene resulting from a rearrangement of the anion analogous to that observed for the imidazolium precursor **4** to **5**, but here involving a deprotonated form of **4**.



Scheme 3 Strategy to access a library of functionalized carbene precursors.

Conclusions

The ability to synthesize three potentially useful carbene precursors starting from the same ethylenediamine species, resulting from an unprecedented intramolecular imidazolium rearrangement and counter-ion effects, offers possibilities for access to a large and varied library of functionalized carbene precursors *via* an atom-economical process (Scheme 3). Such a rearrangement also occurs during the deprotonation of the imidazolium salt. We were able to isolate a carbene-anilide-phenolate zirconium complex showing the ability of a tridentate dianionic carbene ligand to stabilize a hard metal center.

Acknowledgements

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10 Spectroscopic data for **4**: ^{1}H NMR (400 MHz, $CDCl_3$): 9.74 (s, 1H, OH), 8.18 (s, 1H, NCHN), 8.11 (s, 1H, NH), 7.35 (s, 1H, CH_{Ph}), 7.13 (m, 1H, CH_{Ph}), 7.11 (m, 1H, CH_{Ph}), 6.99 (s, 1H, CH_{Ph}), 6.89 (s, 2H, CH_{Mes}), 6.67 (m, 1H, CH_{Ph}), 6.28 (m, 1H, CH_{Ph}), 4.77 (s, 4H, NCH_2), 2.28 (s, 3H, CH_{3Mes}), 2.22 (s, 6H, CH_{3Mes}), 1.41 (s, 9H, *t*Bu), 1.30 (s, 9H, *t*Bu). ^{1}H NMR (500 MHz, MeOH-d_4, −40 °C): 7.43–7.40 (m, 3H, CH), 7.17 (pt, J = 7.2 Hz, 1H, CH), 7.00 (s, 2H, CH), 6.78 (pt, J = 7.2 Hz, 1H, CH), 6.16 (d, J = 8.3 Hz, 1H, CH), 4.56 (m, 2H, NCH_2), 4.45 (m, 2H, NCH_2), 2.32 (s, 3H, CH_{3Mes}), 2.18 (s, 6H, CH_{3Mes}), 1.45 (s, 9H, *t*Bu), 1.33 (s, 9H, *t*Bu). ^{13}C NMR (100 MHz, $CDCl_3$): 158.1 (NCHN), 148.5 (C), 143.9 (C), 143.3 (C), 142.0 (C), 136.4 (C), 135.7 (C), 134.7 (C), 131.3 (CH), 129.4 (CH), 126.6 (CH), 125.3 (C), 125.2 (CH), 120.9 (C), 118.6 (CH), 117.1 (CH), 114.7 (CH), 52.1 (NCH_2), 50.2 (NCH_2), 35.8 (*t*Bu), 34.6 (*t*Bu), 31.6 (*t*Bu), 29.9 (*t*Bu), 21.1 (CH_{3Mes}), 18.7 (CH_{3Mes}).

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12 Spectroscopic data for **5**: ^{1}H NMR (400 MHz, toluene d_8): 11.65 (s, 1H, NCHN), 8.66 (s, 1H, OH), 7.64 (d, J = 8.2 Hz, 1H, CH_{Ph}), 7.13 (t, J = 7.8 Hz, 1H, CH_{Ph}), 6.88 (t, J = 7.8 Hz, 1H, CH_{Ph}), 6.82 (m, 1H, CH_{Ph}), 6.66 (s, 2H, CH_{Mes}), 6.44 (d, J = 8.2 Hz, 1H, CH_{Ph}), 6.33 (br.s, 1H, NH), 6.21 (s, 1H, CH_{Ph}), 5.13 (m, 2H, NCH_2), 3.57 (m, 2H, NCH_2), 2.07 (s, 3H, CH_3), 1.83 (s, 6H, CH_3), 1.65 (s, 9H, *t*Bu), 1.12 (s, 9H, *t*Bu). ^{13}C NMR (100 MHz, toluene-d_8): 147.1 (NCHN), 142.3 (C), 141.6 (C), 140.7 (C), 138.6 (C), 137.2 (C), 136.5 (C), 131.8 (C), 131.3 (C), 129.9 (CH), 126.7 (CH), 126.6 (CH), 125.2 (C), 114.2 (CH), 112.7 (CH), 112.3 (CH), 105.7 (CH), 48.7 (NCH_2), 42.2 (NCH_2), 35.5 (*t*Bu), 34.5 (*t*Bu), 31.9 (*t*Bu), 30.6 (*t*Bu), 21.1 (CH_3), 17.7 (CH_3).

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17 Spectroscopic data for **6**: ^{1}H NMR (400 MHz, acetone-d_6): 10.56 (s, 1H, NCH), 9.58 (s, 1H, NCH), 8.64 (m, 1H, CH_{Ph}), 7.99 (m, 1H, CH_{Ph}), 7.88 (m, 1H, CH_{Ph}), 7.77 (s, 1H, CH_{Ph}), 7.55 (m, 2H, CH_{Mes}), 7.15 (s, 2H, CH_{Ph}), 5.80 (pt, J = 6.1 Hz, 2H, NCH_2), 5.66 (pt, J = 6.1 Hz, 2H, NCH_2), 2.36 (s, 3H, CH_3), 1.71 (s, 6H, CH_3), 1.54 (s, 9H, *t*Bu), 1.16 (s, 9H, *t*Bu). ^{13}C NMR (100 MHz, acetone-d_6): 159.5 (NCH), 154.1 (C), 146.8 (C), 144.9 (NCH), 142.6 (C), 138.3 (C), 136.4 (C), 132.9 (C), 132.2 (C), 130.8 (CH), 130.1 (CH), 129.7 (CH), 129.4 (C), 128.9 (CH), 125.8 (CH), 115.6 (CH), 114.8 (CH), 108.9 (CH), 48.0 (NCH_2), 46.2 (NCH_2), 36.5 (*t*Bu), 35.6 (*t*Bu), 31.5 (*t*Bu), 30.1 (*t*Bu), 21.2 (CH_3), 17.1 (CH_3).

18 For an interesting example of an *N*,*O*-heterocyclic carbene, see: S. Bellemin-Laponnaz, *Polyhedron*, 2010, **29**, 30.

19 A clearer version of the diagram and molecular structures may be found in the ESI (Fig. S2†).

20 (*a*) M. T. Zamora, M. J. Ferguson, R. McDonald and M. Cowie, *Organometallics*, 2012, **31**, 5463; (*b*) T. A. P. Paulose, J. A. Olson, J. W. Quail and S. R. Foley, *J. Organomet. Chem.*, 2008, **693**, 3405; (*c*) S. S. Khan and J. Liebscher, *Synthesis*, 2010, 2609; (*d*) R. Wang, C. M. Jin, B. Twanley and J. M. Shreeve, *Inorg. Chem.*, 2006, **45**, 6396.

21 Spectroscopic data for **7**: ^{1}H NMR (400 MHz, C_6D_6): 6.97 (s, 2H, CH), 6.96 (s, 2H, CH), 6.86 (d, J = 2.1 Hz, 2H, CH), 6.79 (s, 2H, CH), 6.74 (m, 2H, CH), 6.53 (s, 2H, CH), 6.30 (d, J = 8.2 Hz, 2H, CH), 6.06 (d, J = 2.1 Hz, 2H, CH), 4.20 (m, 2H, NCH_2), 3.62 (m, 2H, NCH_2), 3.40 (m, 2H, NCH_2), 2.75 (m, 2H, NCH_2), 2.29 (s, 6H, CH_3), 1.66 (s, 36H, *t*Bu), 1.30 (s, 6H, CH_3), 0.86 (s, 6H, CH_3). ^{13}C NMR (151 MHz, C_6D_6): 200.1 (C_{carb}), 153.6 (C), 152.3 (C), 139.7 (C), 139.5 (C), 138.1 (C), 135.1 (C), 134.4 (C), 133.7 (C), 133.4 (C), 131.4 (CH), 130.9 (C), 128.3 (CH), 124.4 (CH), 124.1 (CH), 111.7 (CH), 111.1 (CH), 110.5 (CH), 104.7 (CH), 50.5 (NCH_2), 47.4 (NCH_2), 35.1 (*t*Bu), 35.0 (*t*Bu), 33.0 (*t*Bu), 30.4 (*t*Bu), 21.3 (CH_3), 17.7 (CH_3), 16.9 (CH_3).

22 The poor quality of the crystals, even after several attempts at recrystallization, precludes accurate determination of parameters.